Memoria del Proyecto de Innovación y Mejora Docente Titulado:

APLICACIÓN DE LA METODOLOGÍA CLIL (CONTENT AND LANGUAGE INTEGRATED LEARNING) EN LA ENSEÑANZA DE LA QUÍMICA CUÁNTICA (Proyecto ID2017/094)

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1 - INTRODUCCIÓN Y JUSTIFICACIÓN DEL PROYECTO

La lengua inglesa constituye el vehículo de comunicación y transferencia de conocimiento por excelencia en todos los campos científicos. Su manejo es, por lo tanto, imprescindible no sólo en el contexto de la investigación sino también en el desarrollo de prácticamente cualquier labor profesional o educativa de ámbito científico.

Pese a esto, hemos comprobado año a año como el nivel de inglés de los estudiantes deja mucho que desear, lo que constituye una enorme limitación a la hora de acceder a la gran mayoría de artículos y libros científicos. Con este problema en mente, y tras haber participado en el "PLAN PILOTO DE INTERNACIONALIZACIÓN DE LOS PROGRAMAS DE ESTUDIO DE LA USAL/DOCENCIA EN INGLÉS", itinerario B, durante el curso académico 2016-2017, decidimos intentar introducir algunos contenidos de la asignatura Química-Física I (2º curso del Grado en Química) utilizando como idioma el inglés.

La Memoria del Grado en Química, donde no se contempla la docencia en idiomas distintos al español, ha restringido nuestras opciones para implementar esta toma de contacto con el inglés científico de manera significativa. A fin de respetar la memoria de grado, decidimos preparar el material de uno de los temas del curso en inglés (aunque la exposición de los contenidos fuera en español) y suministrar bibliografía en inglés a aquellos alumnos que mostraron interés.

2 - OBJETIVOS DEL PROYECTO

Nuestro objetivo ha sido intentar incorporar la lengua científica por excelencia, el inglés, a la docencia de la Química-Física I (2º curso del Grado en Química) mediante la traducción de los materiales y presentaciones correspondientes a uno de los temas del curso ("Orbitales moleculares"). Además de los objetivos académicos intrínsecos a la enseñanza de la materia, intentamos que los estudiantes alcanzaran los siguientes objetivos de naturaleza puramente lingüística:

1. Introducir la terminología inglesa propia de la Mecánica Cuántica

2. Presentar la terminología matemática para discutir en inglés las diferentes ecuaciones que aparecen en el tema.

3. Ilustrar el uso de los conectores lógicos más importantes en inglés. Tales conectores son imprescindibles en cualquier discusión que implique conectar y elaborar ideas.

3 - PLAN DE TRABAJO

El tema elegido para presentar el material en inglés fue el Tema 9 denominado “Moléculas diatómicas”. Su docencia se llevó a cabo durante los días 10, 13, 14 y 20 de noviembre mediante clases magistrales de 1 hora siguiendo el plan presentado en la solicitud del proyecto.

La docencia correspondiente a este tema se apoyó en la discusión de una presentación de power point cuyos contenidos se tradujeron al inglés (la presentación se puede consultar en el Anexo I). Adicionalmente, proporcionamos a los estudiantes numerosa bibliografía estándar en inglés como complemento y soporte de lo explicado en clase.

4 - RESULTADOS

El número de alumnos (150 divididos en 2 grupos) y lo apretado del temario hicieron imposible llevar a cabo ninguna actividad específica de evaluación en inglés. Nuestras impresiones sobre el desarrollo y aprovechamiento de las clases con materiales en inglés se basaron, por lo tanto, en las conversaciones con los alumnos.

Éstas fueron generalmente negativas. En la mayor parte de los casos los estudiantes mostraron su rechazo al empleo del inglés por aumentar, en su opinión, la dificultad de la materia. Tampoco fue bien acogida la opción de emplear bibliografía en inglés, prefiriéndose aquella escrita en castellano, pese a ser menos variada.

5 - ANEXO

En las siguientes páginas se incluye la presentación empleada en las clases teóricas y que constituyó la base sobre la que se apoyaron las clases teóricas.

Diatomic molecules

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Molecular Hamiltonian

Molecule formed by n electrones ($i = 1 \ldots n$) and N nuclei ($\alpha = 1 \ldots N$)

$$\hat{H}(\mathbf{R},\mathbf{r}) \;=\; \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{Ne}(\mathbf{r},\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R})$$

- Kinetic energy terms:

$$\hat{T}_N(\mathbf{R}) \;=\; -\frac{\hbar^2}{2}\sum_{\alpha=1}^{N}\frac{\nabla_\alpha^2}{M_\alpha} \qquad\qquad \hat{T}_e(\mathbf{r}) \;=\; -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2$$

- Electrostatic interactions:

$$\hat{V}_{Ne}(\mathbf{r},\mathbf{R}) \;=\; \sum_{\alpha=1}^{N}\sum_{i=1}^{n} -\frac{Z_\alpha\, e^2}{4\pi\varepsilon_0}\,\frac{1}{r_{i\alpha}}$$

$$\hat{V}_{ee}(\mathbf{r}) \;=\; \sum_{i>j}^{n}\frac{e^2}{4\pi\varepsilon_0}\,\frac{1}{r_{ij}} \qquad\qquad \hat{V}_{NN}(\mathbf{R}) \;=\; \sum_{\alpha>\beta}^{N}\frac{Z_\alpha\, Z_\beta\, e^2}{4\pi\varepsilon_0}\,\frac{1}{R_{\alpha\beta}}$$

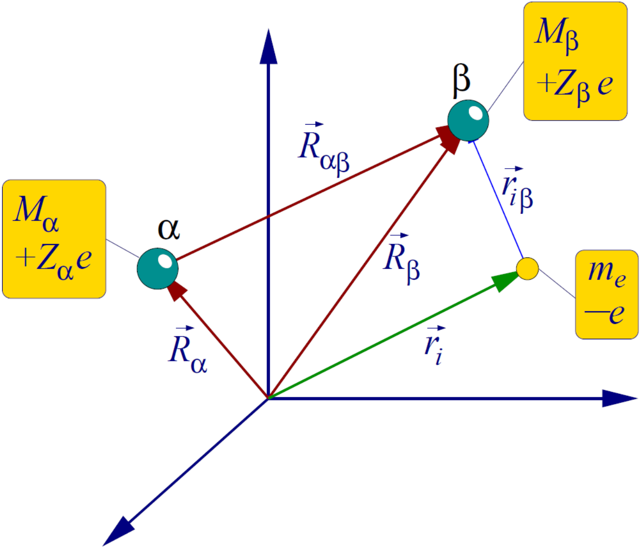
Molecular Hamiltonian

$$\begin{aligned}\hat{H}(\mathbf{R},\mathbf{r}) \quad = \quad & -\frac{\hbar^2}{2}\sum_{\alpha=1}^{N}\frac{\nabla_\alpha^2}{M_\alpha} - \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \sum_{\alpha=1}^{N}\sum_{i=1}^{n}\frac{Z_\alpha\, e^2}{4\pi\varepsilon_0}\frac{1}{r_{i\alpha}} \\ & + \sum_{i>j}^{n}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{ij}} + \sum_{\alpha>\beta}^{N}\frac{Z_\alpha\, Z_\beta\, e^2}{4\pi\varepsilon_0}\frac{1}{R_{\alpha\beta}}\end{aligned}$$

where $r_{i\alpha} = |\vec{R}_\alpha - \vec{r}_i|$, $r_{ij} = |\vec{r}_j - \vec{r}_i|$ y $R_{\alpha\beta} = |\vec{R}_\alpha - \vec{R}_\beta|$ are the electron-nucleus, electron-electron and nucleus-nucleus distances, respectively

- $\mathbf{R} \equiv \{\vec{R}_1 ... \vec{R}_N\}$ y $\mathbf{r} \equiv \{\vec{r}_1 ... \vec{r}_n\}$.

Molecular Hamiltonian



Molecular Hamiltonian

- The wavefunctions that describe the states of molecular systems depend on the electronic and nuclear coordinates. In particular, they are stationary states defined as solutions of the Schrödinger equation:

$$\hat{H}\,\Psi(\mathbf{r},\mathbf{R}) \,=\, E\,\Psi(\mathbf{r},\mathbf{R})$$

- This equation is extremely difficult to solve exactly.
- However, such resolution can be enormously simplified by means of the Born-Oppenheimer approximation, the most important approximation in Quantum-Chemistry.

Born-Oppenheimer approximation

- The Born-Oppenheimer approximation is based on the mass difference between elecrons and nuclei. The second ones are much more heavy and move more slowly than the electrons.
- This makes possible to uncouple (solve separately) the motion of both types of particles.
- The speed of motion of the electrons is so high compared to that of the nuclei that it makes sense to assume that the electrons adapt instantaneously to any nuclear configuration. This means, in other words, that the motion of the electrons can be studied as if the nuclei were stationary by solving the Schrödinger equation for every fixed nuclear geometry.
- At a second stage, and once the electron motion has been characterized, the nuclear motion is studied.The nuclei move in the force of fields (the potential) created by the electrons and obtained by solving the electronic Schrödinger equation for fixed nuclear geometries.

Born-Oppenheimer approximation

- The Born-Oppenheimer approximation assumes that the molecular wavefunction $\Psi(\mathbf{r},\mathbf{R})$ can be written as:

  $$\Psi(\mathbf{r},\mathbf{R}) \approx \Psi^{elec}(\mathbf{r};\mathbf{R})\,\Phi_N(\mathbf{R})$$

  that is, the product of an electronic wavefunction $\Psi^{elec}(\mathbf{r};\mathbf{R})$ that depends on the electronic coordinates and parametrically on the nuclear coordinates and a nuclear wavefunction $\Phi_N(\mathbf{R})$.

Separation of motions

Nuclei mass $>>$ Electrons mass

The electrons perceive the nuclei as if they were frozen, stationary. The electronic motion can be determined for each nuclear geometry and the corresponding wavefunction will be obtained by solving the following equation:

$$\begin{aligned} \hat{H}^{elec}\,\Psi^{elec}(\mathbf{r};\mathbf{R}) &= U(\mathbf{R})\,\Psi^{elec}(\mathbf{r};\mathbf{R}) \\ \hat{H}^{elec} &= \hat{T}_e + \hat{V}_{Ne} + \hat{V}_e + \hat{V}_{NN} \end{aligned}$$

called electronic Schrödinger equation.

Separation of motions

Nuclear motion

Once solved the electronic Schrödinger equation and obtained the function $U(\mathbf{R})$, the motion of the nuclei will be determined by the nuclear Schrödinger equation:

$$(\hat{T}_N(\mathbf{R}) + U(\mathbf{R}))\Phi_N(\mathbf{R}) = E\Phi_N(\mathbf{R})$$

The energy $U(R)$ is, therefore, the potential in which the nuclei move.

Potential energy surface

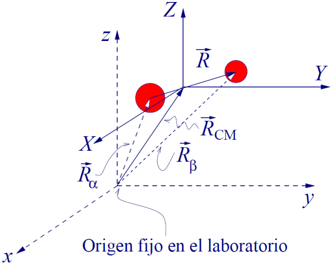
- The function $U(\mathbf{R})$ is the potential, the force field, in which the nuclei move. It is commonly termed as potential energy surface.
- The potential energy surface includes two contributions: the kinetic energy and the nucleus-nucleus repulsion.
- In principle, the potential energy surface depends on $3N$ coordinates. However, the electronic energy can not depend on the 3 coordinates that specify the position of the centre of mass and on the 3 (or 2) coordinates that describe the rotation of the molecule as a whole. In consequence, the potential $U(\mathbf{R})$ depends on $3N-6$ coordinates if the molecule is non lineal and on $3N-5$ if the molecule is lineal.
- The concept of potential energy surface is crucial for the study of spectroscopy and for the study of chemical reactivity.

Nuclear Schrödinger equation for diatomic molecules

$$\left[-\frac{\hbar^2}{2M_\alpha}\nabla^2_\alpha - \frac{\hbar^2}{2M_\beta}\nabla^2_\beta + U(R)\right]\Phi_N(\vec{R}_\alpha,\vec{R}_\beta) = E\Phi_N(\vec{R}_\alpha,\vec{R}_\beta)$$

with $R = |\vec{R}_\beta - \vec{R}_\alpha|$ y $U(R) = E_{elec} + Z_\alpha Z_\beta e^2/R$.

We recast this equation in terms of the vectors:
$\vec{R}_{CM}$ y $\vec{R} = \vec{R}_\beta - \vec{R}_\alpha$
and the masses $M = M_\alpha + M_\beta$ y
$\mu = M_\alpha M_\beta/(M_\alpha + M_\beta)$.



$$\left\{-\frac{\hbar^2}{2M}\nabla^2_{CM} + \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + U(R)\right)\right\}\Phi_N(\vec{R}_{CM},\vec{R}) = E\Phi_N(\vec{R}_{CM},\vec{R})$$

Nuclear Schrödinger equation for diatomic molecules

$$\left\{-\frac{\hbar^2}{2M}\nabla^2_{CM} + \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + U(R)\right)\right\}\Phi_N(\vec{R}_{CM},\vec{R}) = E\Phi_N(\vec{R}_{CM},\vec{R})$$

Separation of motions:

$$\begin{aligned}\Phi_N(\vec{R}_{CM},\vec{R}) &= \varphi_{tr}(\vec{R}_{CM})\varphi_{int}(\vec{R}) \\ E &= E_{tr} + E_{int}\end{aligned}$$

- Displacement of the system as a whole:

$$-\frac{\hbar^2}{2M}\nabla^2_{CM}\,\varphi_{tr}(\vec{R}_{CM}) = E_{tr}\varphi_{tr}(\vec{R}_{CM})$$

Free particle E_{tr} is not quantized.

Nuclear Schrödinger equation for diatomic molecules

- Internal motion:

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + U(R)\right)\varphi_{int}(\vec{R}) = E_{int}\varphi_{int}(\vec{R})$$

  $U(R)$ is central → spherical coordinates
  Central field problem:

$$\varphi_{int}(\vec{R}) = F(R)Y_{JM}(\theta,\phi)$$

  where the angular functions $Y_{JM}(\theta,\phi)$ are spherical harmonics.

The equation for the internal motion only depends on R:

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dR^2} + \frac{2}{R}\frac{d}{dR}\right)F(R) + \left(\frac{J(J+1)\hbar^2}{2\mu R^2} + U(R)\right)F(R) = E_{int}F(R)$$

Nuclear Schrödinger equation for diatomic molecules

If we define $G(R) = RF(R)$:

$$-\frac{\hbar^2}{2\mu}G''(R) + \left(\frac{J(J+1)\hbar^2}{2\mu R^2} + U(R) - E_{int}\right)G(R) = 0$$

- We need a functional form for $U(R)$. It is common practice to use a Taylor series centered at $R = R_e$ or, alternatively, simple analytical functions.
- The term $1/R^2$ also can be expressed as a Taylor series.
- Depending on how such contributions are dealt with and how the series are truncated, we will find different models (harmonic oscillator-rigid rotor, 7 parameters,...).
- In any case, the states are always characterized by means of three quantum numbers: vibrational, rotational (J) and azimuthal (M_J).

$\hookrightarrow$ Spectroscopy

Electronic Hamiltonian for a diatomic molecule

For a diatomic molecule, the electronic Schrödinger equation is:

$$\begin{aligned}
\hat{\mathcal{H}}^{elec}\,\Psi^{elec}(\mathbf{r};R) &= U(R)\,\Psi^{elec}(\mathbf{r};R)\\
\hat{\mathcal{H}}^{elec} &= \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}\\
&= -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\hat{\nabla}_i^2 - \sum_{i=1}^{n}\frac{Z_\alpha e^2}{4\pi\varepsilon_0 r_{i\alpha}} - \sum_{i=1}^{n}\frac{Z_\beta e^2}{4\pi\varepsilon_0 r_{i\beta}}\\
&\quad + \sum_{i>j}^{n}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0 R}
\end{aligned}$$

Molecular orbitals method

- As in the atomic case, the term describing the electron-electron repulsion is responsible for most of the difficulties involved in the resolution of the electronic Schrödinger equation and for the necessity to look for approximations that simplify the problem.
- To this end, we studied multi-electron atoms by means of independent particle models based on the orbital approximation. In these models, the electron-electron repulsion was either neglected, represented by means of an effective charge or averaged (Hartree-Fock method), in such a way that we could define monoelectronic wavefunctions called orbitals and whose sequential occupation by the electrons gave rise to the electronic configuration.
- The strategy that we will follow to solve the electronic problem in molecules is exactly the same; we will work in the context of the orbital and independent particle approximations.

Molecular orbitals method

- The extension of the atomic orbital idea to the molecular case makes possible to define molecular orbitals.
- The molecular orbitals are monoelectronic wavefunctions spread over all the nuclei forming the molecule. Their square represents the probability density of finding the electron occupying the orbital in a certain position of the space.
- The molecular electronic wavefunction $\Psi^{elec}(\mathbf{r}; R)$ will be expressed as an antisymmetrized product of molecular orbitals (a Slater determinant).
- The "best" molecular orbitals for a certain problem are those calculated through the Hartree-Fock methodology.

Molecular orbitals method

- The "best" molecular orbitals for a certain problem are those calculated through the Hartree-Fock methodology.
- Application of the Hartree-Fock method to molecules is almost identical to the atomic case. The only difference stems from the fact that, in the molecular case, the central field approximation can not be invoked. In its place, the LCAO ("Linear Combination of Atomic Orbitals") is applied. In the LCAO approximation, the spatial part of the molecular orbitals is written as a linear combination of atomic orbitals corresponding to the atoms forming the molecule. When the electronic energy is optimized as a function of the expansion coefficients, we obtain the Roothann equations, the equations at the core of the application of the Hartree-Fock method to molecules.
- As in the atomic case:
  - The Hartree-Fock method makes possible to define an electronic molecular configuration.
  - The Hartree-Fock method does not account for the correlation energy properly.

Commuting operators with $\hat{\mathcal{H}}^{elec}$

- Proper definition of molecular electronic configurations precise to determine the operators which commute with the electronic Hamiltonian in the context of the independent particle approximation.
- $\hat{\mathcal{H}}^{elec}$ does not involve any spin operator and therefore commutes with $\hat{S}^2$, $\hat{S}_z$, $\hat{s}^2$ and $\hat{s}_z$.

$$\left[\hat{\mathcal{H}}^{elec}, \hat{S}^2\right] = 0 \qquad \left[\hat{\mathcal{H}}^{elec}, \hat{S}_z\right] = 0$$

$$\left[\hat{\mathcal{H}}^{elec}, \hat{s}^2\right] = 0 \qquad \left[\hat{\mathcal{H}}^{elec}, \hat{s}_z\right] = 0$$

- A diatomic molecule (or linear) has cylindrical symmetry: $\hat{L}^2$ (or $\hat{l}^2$) does not commute with the electronic Hamiltonian. However, the operators corresponding to the projection of the total and individual orbital angular momentum on the internuclear axis do commute with $\hat{\mathcal{H}}^{elec}$:

$$\left[\hat{\mathcal{H}}^{elec}, \hat{L}_z\right] = 0 \quad \left[\hat{\mathcal{H}}^{elec}, \hat{l}_z\right] = 0$$

As it happened in the atomic case, $\hat{l}^2$ and $\hat{l}_z$ would not commute with the electronic Hamiltonian if we were not working in the context of the independent particle approximation.

Commuting operators with $\hat{\mathcal{H}}^{elec}$

- A diatomic molecule (or linear) has cylindrical symmetry: $\hat{L}^2$ (or $\hat{l}^2$) do not commute with the electronic Hamiltonian. However, the operators corresponding to the projection of the total and individual orbital angular momentum on the internuclear axis do commute:

  $$\left[\hat{\mathcal{H}}^{elec}, \hat{L}_z\right] = 0 \quad \left[\hat{\mathcal{H}}^{elec}, \hat{l}_z\right] = 0$$

  The eigenvalues of $\hat{l}_z$ are $m_l = 0, \pm 1, \pm 2 ....$ The quantum number $\lambda = |m_l|$ is used to label the molecular orbitals of diatomic molecules (and linear molecules in general). The molecular orbitals are labelled by means of a greek letter that depends on the value of λ: $\sigma(\lambda = 0), \pi(\lambda = 1), \delta(\lambda = 2), \phi(\lambda = 3), ...$ Many different orbitals corresponding to the same type may exist, in which case they are indicated as 1σ, 2σ, 3σ, etc (for the σ case). Those molecular orbitals characterized by $\lambda \neq 0$ are doubly degenerated ($m_l = +\lambda, -\lambda$).

- The molecular orbitals of diatomic molecules can be labeled as g o u depending on whether they are symetric or antisymmetric with respect to the inversion centre.

- The electronic wavefunction ($\Psi^{elec}(\mathbf{r}; R)$) can be built from the molecular orbitals using a Slater determinant as functional form.

Commuting operators with $\hat{\mathcal{H}}^{elec}$

- As in the atomic case, a single electronic configuration is not well suited to represent the electronic states beyond the independent particle models. The proper way of representing such states is through terms which, in this case, will be characterized by means of the quantum numbers S and M_L. The terms can be calculated from the electronic configurations and split according to the Hund's rules.
- In linear molecules, capital greek letters are used to $(\Sigma, \Pi, \Delta,\ \Phi, ...)$ indicate the absolute value of the total angular momentum proyection $(\Lambda = |M_L|)$ on the internuclear axis. These symbols are used to label the molecular electronic states for linear molecules. The absolute value is employed because the electronic energy depends on M_L^2. Those levels characterized by a value of Λ different from zero will be doubly degenerated as $M_L = \pm\Lambda$.

Commuting operators with $\hat{\mathcal{H}}^{elec}$

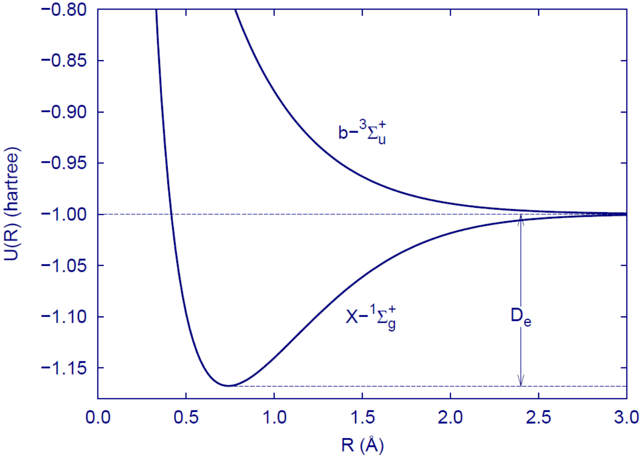
- $\hat{\mathcal{H}}^{elec}$ will also commute with the symmetry operators corresponding to the molecular point group:
    - If $\hat{i}$ is a symmetry operation: states with eigenvalues $+1(-1)$ will be indicated as *gerade* (*ungerade*) and labelled with the subindex g (u).
    - If vertical planes σ_v exist: states with eigenvalues $+1(-1)$ will be labelled with the superindex $+$ $(-)$.

$\hookrightarrow$ The electronic states of diatomic molecules are designated though the labels corresponding to the electronic terms:

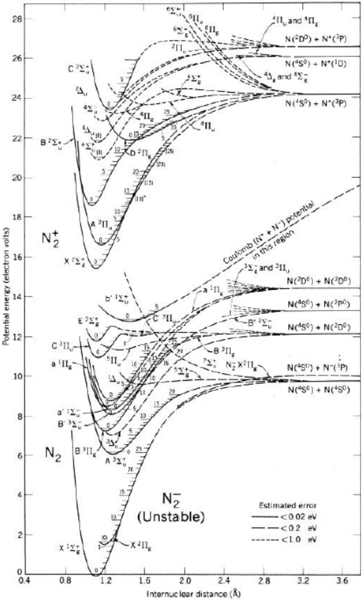
$$\text{etiqueta} -^{2S+1}\Lambda^{+|-}_{g|u}$$

The spin-orbit interaction has been neglected and will not be considered.

Electronic states of a molecule



Electronic states of a molecule



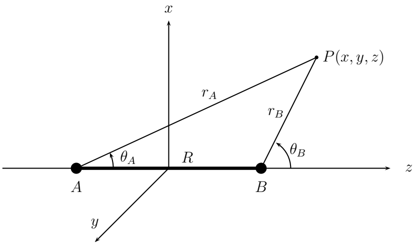
H_2^+ ion

System formed by one electron and two nuclei: the electronic Schrödinger equation can be solved **exactly**.

$$\begin{aligned}\hat{\mathcal{H}}^{elec} &= -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Z_A e^2}{4\pi\epsilon_0 r_A} - \frac{Z_B e^2}{4\pi\epsilon_0 r_B} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} \\ &= \hat{T} + \hat{V}_A(r_A) + \hat{V}_B(r_B) + \hat{V}_{AB}(R)\end{aligned}$$

H_2^+ ion. Exact solution in elliptic coordinates.

- Elliptical coordinates are used to solve the problem:



$$\lambda = \frac{1}{R}\,(r_A + r_B) \qquad 1 \leq \lambda \leq \infty$$

$$\mu = \frac{1}{R}\,(r_A - r_B) \qquad -1 \leq \mu \leq +1$$

$$\phi \qquad 0 \leq \phi < 2\pi$$

$$r_A = \frac{R}{2}\,(\lambda + \mu)$$

$$r_B = \frac{R}{2}\,(\lambda - \mu)$$

H_2^+ ion. Exact solution in elliptic coordinates.

In elliptical coordinates and atomic units, the electronic Schrödinger equation for the H_2^+ ion can be written as:

$$\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial\psi_e}{\partial\lambda}\right]+\frac{\partial}{\partial\mu}\left[(\mu^2-1)\frac{\partial\psi_e}{\partial\mu}\right]+\left[\frac{1}{\lambda^2-1}+\frac{1}{1-\mu^2}\right]\frac{\partial^2\psi_e}{\partial\phi^2} + \left[\frac{R^2E}{2}(\lambda^2-\mu^2)+2R\lambda\right]\psi_e=0$$

It is possible to separate variables, in such a way that the solution can be written as:

$$\psi^{elec}(\lambda,\mu,\phi) = \Lambda(\lambda)H(\mu)e^{im\phi} \quad m=0,\pm1,\pm2,\ldots$$

And the problem gets reduced to three differential equations on a single variable that can be solved exactly for each internuclear distance R.

H_2^+ ion. Exact solution in elliptic coordinates.

When the electronic problem is solved exactly it is found that the electronic ground state shows a 2.79 eV minimum at a distance 1.06 Å.

H_2^+ ion. Exact solution in elliptic coordinates.

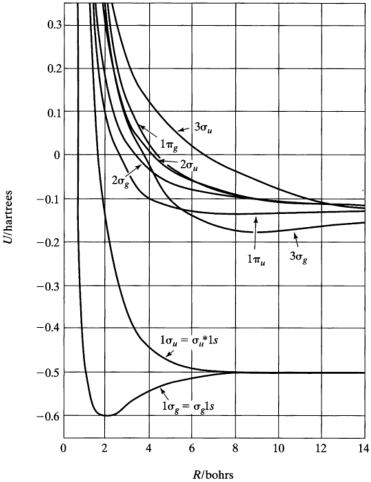


FIGURE 13.5 $U(R)$ curves for several H_2^+ electronic states. [Curves taken from J. C. Slater, *Quantum Theory of Molecules and Solids,* vol. 1, McGraw-Hill, 1963. Used by permission.]

H_2^+ ion. Molecular orbitals-LCAO

We will use an approximated treatment based on the molecular orbitals-LCAO method. It seems reasonable to write the two lowest-energy molecular orbitals as linear combinations of the $1s$ atomic orbitals supported by the hydrogen atoms forming the molecule. The two molecular orbitals so obtained will have σ symmetry.

We will indicate the $1s$ atomic orbitals as χ_A and χ_B, depending on the nucleus (A or B) they are centered at:

$$\chi_A \equiv a = \sqrt{\frac{\xi^3}{\pi a_0^3}} e^{\frac{-\xi \, r_A}{a_0}} \qquad \chi_B \equiv b = \sqrt{\frac{\xi^3}{\pi a_0^2}} e^{\frac{-\xi \, r_B}{a_0}}$$

As only one electron is forming the molecule, the total electronic wavefunction will coincide with a single molecular orbital. Therefore, the spatial part will be given by:

$$\psi^{elec} = c_1 \, a + c_2 \, b$$

H_2^+ ion. Molecular orbitals-LCAO

Optimizing $\langle\psi|\hat{H}^{elec}|\psi\rangle$ with respect to c_1 and c_2 (Rayleigh-Ritz's method) for any value of the distance R leads us to the following approximated wavefunction for the two lowest-energy molecular orbitals:

$$\sigma_g = \frac{a+b}{\sqrt{2(1+S)}} \qquad \sigma_u = \frac{a-b}{\sqrt{2(1-S)}}$$

where their symmetry is explicitly indicated and $S = \langle a|b\rangle$.

H_2^+ ion. Molecular orbitals-LCAO

When plotting the energies $U(R)$ corresponding to σ_g and σ_u for each internuclear distance R we get the following curves:

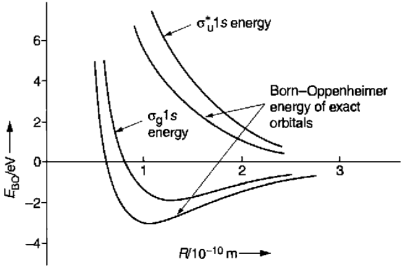
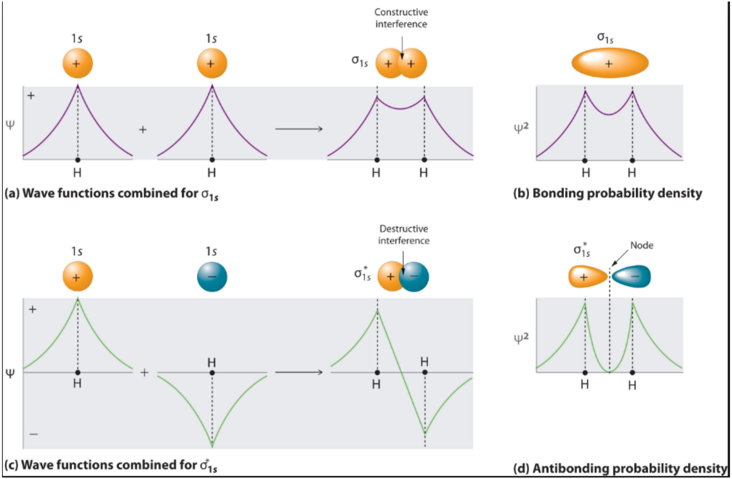


Figure 18.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. This diagram shows qualitatively how the Born–Oppenheimer energies of the LCAO molecular orbitals compare with the Born Oppenheimer energies of the "exact" orbitals. The approximate orbital energies must lie above the corresponding exact energies for all internuclear distances.

H_2^+ ion. Molecular orbitals-LCAO

- The orbital σ_g is called "bonding" because it leads to the formation of a chemical bond ($R_e = 1.34$ eV, depth=1.76 eV).
- The orbital σ_u is said to be "antibonding" because it displays a repulsive character for any internuclear distance R.
- The results could be improved by including more base functions (atomic orbitals) with the right symmetry (p_z, for instance) in the expansion of the molecular orbitals.

H_2^+ ion. Molecular orbitals-LCAO



H_2 molecule

System formed by two electrons and two nuclei: the electronic Schrödinger equation can not be solved exactly due to the electronic repulsion.

$$\begin{aligned}\hat{\mathcal{H}}^{elec} &= -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Z_A e^2}{4\pi\epsilon_0 r_A} - \frac{Z_B e^2}{4\pi\epsilon_0 r_B} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \\ &= \hat{T} + \hat{V}_A(r_A) + \hat{V}_B(r_B) + \hat{V}_{AB}(R) + \hat{V}_{ee}(r_{12})\end{aligned}$$

We will use an approximated method to solve the problem: the molecular-orbitals method.

H_2 molecule. Molecular orbitals.

The electronic wavefunction for the electronic ground state will be given by the following Slater determinant:

$$\psi^{elec} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) \end{vmatrix}$$

where, following the Hartree-Fock methodology, ψ_1 is a molecular orbital chosen so that the energy:

$$\langle \psi^{elec} | \hat{H}^{elec} | \psi^{elec} \rangle$$

gets minimum for each internuclear distance R. In order to perform the optimization of the energy, the orbital ψ_1 will be expressed as a linear combination of atomic orbitals (Roothaan method). For instance,

$$\psi_1 = c_a\,\chi_a + c_b\,\chi_b$$

if we only considered two atomic functions, χ_a (centered at the atom a) y χ_b (centered at the atom b).

H_2 molecule. Molecular orbitals.

Instead of performing the calculation following the Hartree-Fock methodology and the Roothaan equations, we will make use of an approximated treatment that mimics that employed for the H_2^+ molecule. Qualitatively speaking, one could expect that the lowest-energy orbitals for the H_2 molecule will be those obtained by combining the lowest-energy atomic orbitals centered at the hydrogen atoms:

$$\chi_A \equiv a = \sqrt{\frac{\xi^3}{\pi a_0^3}} e^{\frac{-\xi\, r_A}{a_0}} \qquad \chi_B \equiv b = \sqrt{\frac{\xi^3}{\pi a_0^2}} e^{\frac{-\xi\, r_B}{a_0}}$$

As in the H_2^+ case, the linear combinations of the $1s$ orbitals will generate a σ_g molecular orbital that displays a minimum at a certain value of the internuclear distance R and an antibonding molecular orbital σ_u of higher energy.

$$\sigma_g = \frac{a+b}{\sqrt{2(1+S)}} \qquad \sigma_u = \frac{a-b}{\sqrt{2(1-S)}}$$

(The Hartree-Fock method and the Roothan equations would lead to this result as well if we used a y b as the only basis functions in the expansion of the molecular orbitals.)

H_2 molecule. Molecular orbitals.

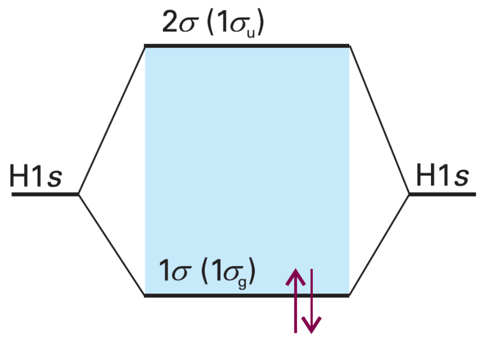
The two electrons will occupy the lowest-energy molecular orbital, in such a way that the approximated electronic wavefunction will be given by:

$$\psi^{elec} = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_g(1)\beta(1) \\ \sigma_g(2)\alpha(2) & \sigma_g(2)\beta(2) \end{vmatrix} = \sigma_g(1)\sigma_g(2)\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

which corresponds to the electronic configuration σ_g^2 o $1\sigma_g^2$. If we evaluate the expected value of the electronic Hamiltonian for this wavefunctions and different internuclear distances, it is found that the energy displays a minimum at 0.85Å whose depth is 2.65 eV.

The error is significant and these results are quite far from the experimental ones. They could be improved by increasing the number of atomic functions. It should not be forgotten though that the Hartree-Fock methodology and the molecular orbitals it renders represent an independent particle approach that will never manage to reproduce the experimental results exactly as it does not account for the correlation energy properly.

H_2 molecule. Molecular orbitals.



Hydrogen-like atoms

H (1 electron)

- Spin-orbitals for hydrogen-like atoms: eigenfunctions of $\hat{h}$, $\hat{l}^2$, $\hat{l}_z$, $\hat{s}^2$, $\hat{s}_z$

$$\chi_{nln_lm_s} = R_{nl}(r)Y_{lm_l}(\theta,\phi)\omega \qquad (\omega = \alpha \text{ o } \omega = \beta)$$

- Degeneracy: $\varepsilon = \varepsilon_n$
  Spin-orbitals in the same shell: $2n^2$

Multi-electron atoms

Atoms with more than 1 electron. Hartree-Fock approximation.)

- Atomic spin-orbitals: eigenfunctions of $\hat{f}$, $\hat{l}^2$, $\hat{l}_z$, $\hat{s}^2$, $\hat{s}_z$

$$\chi'_{nln_lm_s} = R'_{nl}(r)Y_{lm_l}(\theta,\phi)\omega \qquad (\omega = \alpha \text{ o } \omega = \beta)$$

  Central field approximation

- Degeneracy: $\varepsilon = \varepsilon_{nl}$
  Orbitals in the same subshell: $2l+1$
  Spin-orbitals in the same subshell: $2(2l+1)$
- Each electronic state is described through a Slater determinant formed by the occupied spin-orbitals.
- It is possible to define electronic configurations. In general, more than one atomic state corresponds to each configuration (when these are indicated through the filled and half-filled subshells without specifying m_l and m_s).

Single-electron diatomic molecules

H_2^+ (1 electron)

- Molecular orbitals: eigenfunctions of $\hat{h}$, $\hat{l}_z$, $\hat{O}_I$, $\hat{O}_{\sigma_v}$ (the two lowest-energy orbitals are labelled as $1\sigma_g^+$ and $1\sigma_u^+$, respectively).
- Degeneracy: $\varepsilon = \varepsilon(\lambda)$
  Orbitals in the same molecular subshell: 1 (λ=0) o 2 ($\lambda \neq 0$)

Multi-electron diatomic molecules

Molecules formed by more than one electron. Hartree-Fock approximation.

- Molecular orbitals: eigenfunctions of $\hat{f}$, $\hat{l}_z$, $\hat{O}_{\sigma_v}$ (and $\hat{O}_I$ for homonuclear molecules)
  LCAO approximation.
- Degeneracy: $\varepsilon = \varepsilon(\lambda)$
  Orbitals in the same molecular subshell: 1 (λ=0) o 2 ($\lambda \neq 0$)
- Each electronic state is described through a Slater determinant formed by the occupied spin-orbitals.
- It is possible to define molecular electronic configurations. In general, more than one molecular state corresponds to each configuration (when these are indicated through the filled and half-filled subshells without specifying m_l and m_s).

First and second period diatomic molecules.

Molecular orbitals methodology

- For the diatomic molecules formed by atoms belonging to the first and second period, the molecular orbitals can be formed using the Hartree-Fock methodology in combination with the LCAO approximation. The atomic orbitals $1s$, $2s$, $2p_x$, $2p_y$ y $2p_z$ are used as basis functions.
- It can be proved that the value of λ ($|m_l|$) determines the symmetry of the molecular orbitals. In particular, such symmetry depends on the number of nodal planes that cross at the internuclear axis.
- Application of the Hartree-Fock methodology shows that only those atomic orbitals with the same symmetry mix with each other. This means, for example, that only the atomic orbitals $1s$, $2s$ y $2p_z$ will contribute to the molecular orbitals σ. Accordingly, only the atomic orbitals $2p_x$ y $2p_y$ will mix to form the π molecular orbitals.
- Besides, the analysis of the results from Hartree-Fock calculations show that those atomic orbitals with the same symmetry and similar energies mix more intensely than those orbitals with equal symmetry but very different energies.

Homonuclear diatomic molecules

If only the mixing between equivalent atomic orbitals of the same symmetry is allowed, the diagram of molecular orbitals for a homonuclear diatomic molecule would be:

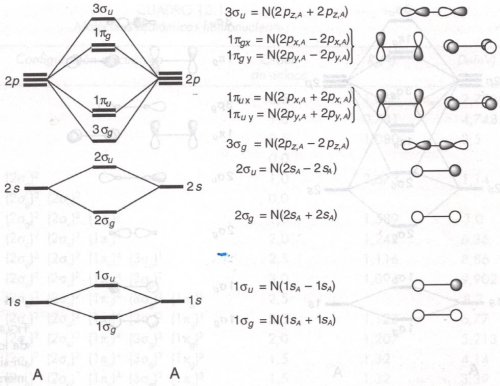


FIGURA 10.1. Diagrama energético de los orbitales moleculares para un sistema A_2 teniendo en cuenta únicamente la interacción de orbitales equivalentes.

Homonuclear diatomic molecules

If the former restriction is lifted up and we allow for the mixing of the atomic orbitals $2s_A$, $2s_B$, $2p_{zA}$ y $2p_{zB}$ into the molecular orbitals $2\sigma_g$, $2\sigma_u$, $3\sigma_g$ y $3\sigma_u$, the diagram changes slightly:

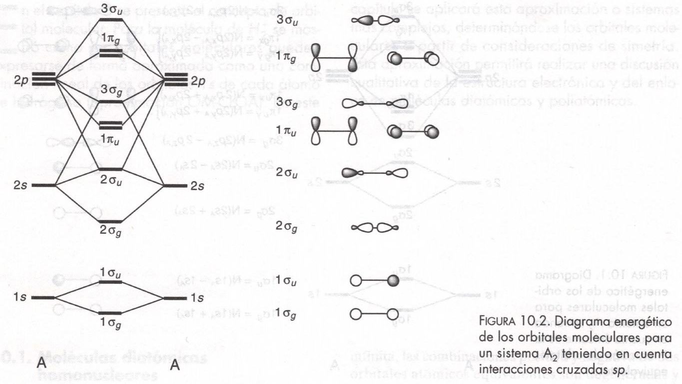
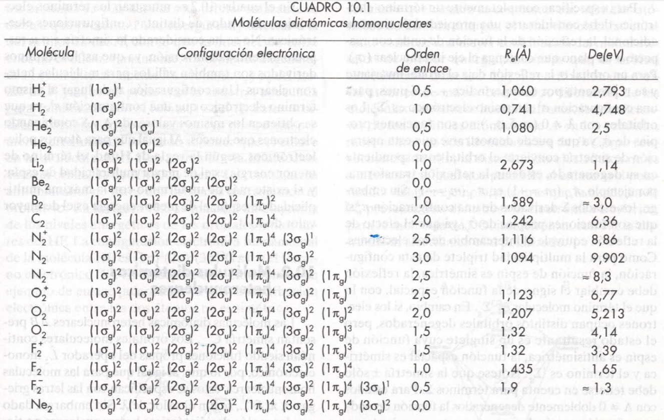


FIGURA 10.2. Diagrama energético de los orbitales moleculares para un sistema A_2 teniendo en cuenta interacciones cruzadas *sp*.

Homonuclear diatomic molecules

Electronic configuration

The electronic configuration for the ground electronic state can be obtained "filling" the molecular orbitals with the N electrons that form the molecule according to their energy and following Pauli's exclusion principle.



CUADRO 10.1

Moléculas diatómicas homonucleares

Molécula	*Configuración electrónica*	*Orden de enlace*	*$R_e(\text{Å})$*	*De(eV)*
H_2^+	$(1\sigma_g)^1$	0,5	1,060	2,793
H_2	$(1\sigma_g)^2$	1,0	0,741	4,748
He_2^+	$(1\sigma_g)^2\ (1\sigma_u)^1$	0,5	1,080	2,5
He_2	$(1\sigma_g)^2\ (1\sigma_u)^2$	0,0		
Li_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2$	1,0	2,673	1,14
Be_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2$	0,0		
B_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^2$	1,0	1,589	≈ 3,0
C_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4$	2,0	1,242	6,36
N_2^+	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^1$	2,5	1,116	8,86
N_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2$	3,0	1,094	9,902
N_2^-	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^1$	2,5		≈ 8,3
O_2^+	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^1$	2,5	1,123	6,77
O_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^2$	2,0	1,207	5,213
O_2^-	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^3$	1,5	1,32	4,14
F_2^+	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^3$	1,5	1,32	3,39
F_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^4$	1,0	1,435	1,65
F_2^-	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^4\ (3\sigma_u)^1$	0,5	1,9	≈ 1,3
Ne_2	$(1\sigma_g)^2\ (1\sigma_u)^2\ (2\sigma_g)^2\ (2\sigma_u)^2\ (1\pi_u)^4\ (3\sigma_g)^2\ (1\pi_g)^4\ (3\sigma_u)^2$	0,0		

Heteronuclear diatomic molecules

Molecular orbitals method

- Our former discussion about homonuclear molecules can be applied verbatim to their heteronuclear counterparts, except for the fact that heteronuclear molecules do not have inversion centre and the molecular orbitals can not be labelled with the subindexes g o u.
- The expansion coefficients for equivalent atomic orbitals will not be the same now. In general, when different atomic orbitals of the same symmetry combine each other to produce molecular orbitals, the lowest (highest) atomic orbitals contribute predominantly to the bonding (antibonding) molecular orbitals. As a consequence of this, the bonds polarize.

Heteronuclear diatomic molecules

no electrónico $^1\Sigma^+$. El enlace en esta molécula es un ejemplo de enlace polarizado, ya que la distribución electrónica entre los dos átomos no es simétrica.

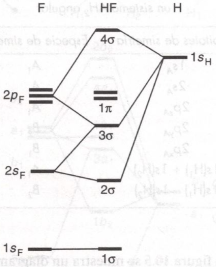


FIGURA 10.3. Diagrama energético de los orbitales moleculares de la molécula HF.

Para moléculas diatómicas heteronucleares formadas por átomos del segundo periodo, el diagrama

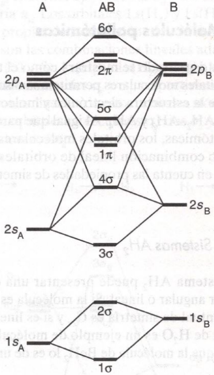
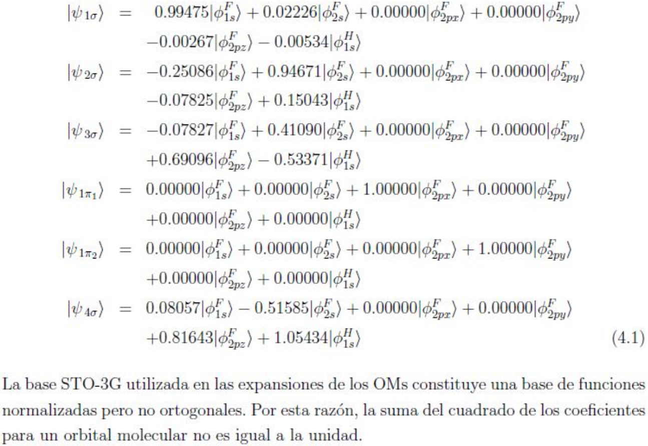


FIGURA 10.4. Diagrama energético de los orbitales moleculares de un sistema *AB* en el que el átomo *A* es más electronegativo que *B*.

Heteronuclear diatomic molecules



$$\begin{aligned}
|\psi_{1\sigma}\rangle &= 0.99475|\phi^F_{1s}\rangle + 0.02226|\phi^F_{2s}\rangle + 0.00000|\phi^F_{2px}\rangle + 0.00000|\phi^F_{2py}\rangle \\
&\quad -0.00267|\phi^F_{2pz}\rangle - 0.00534|\phi^H_{1s}\rangle \\
|\psi_{2\sigma}\rangle &= -0.25086|\phi^F_{1s}\rangle + 0.94671|\phi^F_{2s}\rangle + 0.00000|\phi^F_{2px}\rangle + 0.00000|\phi^F_{2py}\rangle \\
&\quad -0.07825|\phi^F_{2pz}\rangle + 0.15043|\phi^H_{1s}\rangle \\
|\psi_{3\sigma}\rangle &= -0.07827|\phi^F_{1s}\rangle + 0.41090|\phi^F_{2s}\rangle + 0.00000|\phi^F_{2px}\rangle + 0.00000|\phi^F_{2py}\rangle \\
&\quad +0.69096|\phi^F_{2pz}\rangle - 0.53371|\phi^H_{1s}\rangle \\
|\psi_{1\pi_1}\rangle &= 0.00000|\phi^F_{1s}\rangle + 0.00000|\phi^F_{2s}\rangle + 1.00000|\phi^F_{2px}\rangle + 0.00000|\phi^F_{2py}\rangle \\
&\quad +0.00000|\phi^F_{2pz}\rangle + 0.00000|\phi^H_{1s}\rangle \\
|\psi_{1\pi_2}\rangle &= 0.00000|\phi^F_{1s}\rangle + 0.00000|\phi^F_{2s}\rangle + 0.00000|\phi^F_{2px}\rangle + 1.00000|\phi^F_{2py}\rangle \\
&\quad +0.00000|\phi^F_{2pz}\rangle + 0.00000|\phi^H_{1s}\rangle \\
|\psi_{4\sigma}\rangle &= 0.08057|\phi^F_{1s}\rangle - 0.51585|\phi^F_{2s}\rangle + 0.00000|\phi^F_{2px}\rangle + 0.00000|\phi^F_{2py}\rangle \\
&\quad +0.81643|\phi^F_{2pz}\rangle + 1.05434|\phi^H_{1s}\rangle
\end{aligned} \tag{4.1}$$

La base STO-3G utilizada en las expansiones de los OMs constituye una base de funciones normalizadas pero no ortogonales. Por esta razón, la suma del cuadrado de los coeficientes para un orbital molecular no es igual a la unidad.

Heteronuclear diatomic molecules

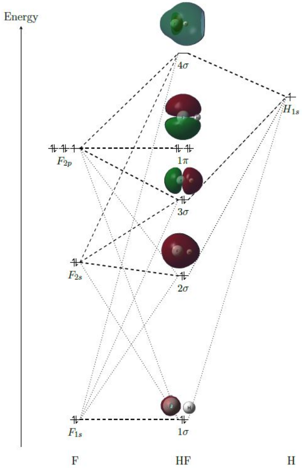


Figura 4.1: Diagrama de orbitales moleculares para la distancia internuclear de equilibrio del HF obtenido mediante un cálculo tipo Hartree-Fock con la base STO-3G. En el diagrama solo se representa uno de los dos orbitales π degenerados perpendiculares entre sí.

Electronic terms

- The electronic energy levels of molecules are not represented by means of configurations but terms. As a matter of fact, electronic configurations only make sense in the context of the independent particle models. When going beyond these models in order to recover the correlation energy, the idea of electronic configuration does not longer applies. However, this is not the case for the terms.
- It is therefore important to be able to determine the terms compatible with a given electronic configuration. Following the discussion of the atomic case, we can use the ground electronic configuration of the molecule to determine the terms compatible with such configuration. These terms will continue representing the molecular energy levels even in those situations when we move further from the independent particle models.

Electronic terms

- The electronic levels for a diatomic molecule are indicated through terms:

$$\text{label} -{}^{2S+1}\,\Lambda_{g|u}^{+|-}$$

- The electronic Hamiltonian commutes with the operators $\hat{L}_z$ and $\hat{S}^2$. The quantum numbers M_L and S are used to label the terms through $\Lambda = |M_L|$ and the multiplicity $2S+1$.
- The symbols $+/-$ y g/u indicate the behaviour of the electronic wavefunction under reflexion through a vertical plane or through inversion, respectively.

Electronic terms

- The electronic levels for a diatomic molecule are indicated through terms:

$$\text{label} -^{2S+1}\Lambda_{g|u}^{+|-}$$

- M_L is obtained by summing the values of the individual projections m for each of the electrons forming the molecule. As for the molecular orbitals, Λ will be represented by means of a greek letter:

Λ	0	1	2	3	4
Symbol	Σ	Π	Δ	Φ	Γ

  Those states with values of $\Lambda \neq 0$ will be doubly degenerated as $M_L = \pm\Lambda$ and the electronic energy just depends on M_L^2. The total degeneracy, including that due to spin, is:

$$g_{\Lambda=0} = 2S+1 \quad g_{\Lambda\neq 0} = 2(2S+1)$$

- For closed molecular subshells, $S = \Lambda = 0$ and the only possible term is $^1\Sigma$. In consequence, we will just have to focus on the half-filled molecular subshells.

Electronic terms

- The electronic levels for a diatomic molecule are indicated through terms:

$$\text{label} -^{2S+1}\,\Lambda^{+|-}_{g|u}$$

- Disregarding the electronic correlation, all terms corresponding to the same configuration are degenerated. However, when the electronic correlation is considered, the degeneracy is lifted according to the Hund's rules: the term with the largest degeneracy correlates with the lowest energy and, in case of having several terms with the same multiplicity, the term characterized by the largest value of Λ will possess the lowest energy.

Terms corresponding to non-equivalent electrons

All (no restrictions) possible values of Λ and S are combined into terms.

Example: electronic configuration $\pi^1\pi^1$

1. Possible values of $M_L = m_{l1} + m_{l2}$

m_{l1}	m_{l2}	M_L
+1	+1	+2
-1	-1	-2
+1	-1	0
-1	+1	0

- One term $\Delta \Leftrightarrow |\Lambda| = 2 \quad (M_L = \pm 2)$.
- Two terms Σ, one for each $\Lambda = 0 \quad (M_L = 0)$.

2. Possible values of $M_S = m_{s,1} + m_{s,2}$

$m_{s,1}$	$m_{s,2}$	M_S
+1/2	+1/2	+1
-1/2	-1/2	-1
+1/2	-1/2	0
-1/2	+1/2	0

- One triplet $S = 1 \Leftrightarrow M_S = +1, 0, -1$.
- One singlet $S = 0 \Leftrightarrow M_S = 0$.

Terms corresponding to non-equivalent electrons

Example: electronic configuration $\pi^1\pi^1$

We have:

- One term Δ
- Two terms Σ
- One triplet $S = 1$
- One singlet $S = 0$

$\hookrightarrow$ Six possible terms:

$$^3\Delta,\ ^3\Sigma,\ ^3\Sigma,\ ^1\Delta,\ ^1\Sigma,\ ^1\Sigma$$

Terms corresponding to equivalent electrons

Only those values of Λ and S that fulfill the exclusion principle are combined into terms.

Example: electronic configuration π^2

1. Possible values of $M_L = m_{l1} + m_{l2}$ y $M_S = m_{s,1} + m_{s,2}$

m_{l1}	$m_{s,1}$	m_{l2}	$m_{s,2}$	M_L	M_S
+1	1/2	+1	-1/2	+2	0
+1	1/2	-1	1/2	0	1
+1	1/2	-1	-1/2	0	0
+1	-1/2	-1	1/2	0	0
+1	-1/2	-1	-1/2	0	-1
-1	1/2	-1	-1/2	-2	0

2. Rows with the same value of $|\Lambda|$:
   - $|\Lambda| = 2$ y $M_S = 0 \Rightarrow {}^1\Delta$
   - $|\Lambda| = 0 \Rightarrow \Sigma$
3. Gather terms with M_S:
   - $M_S = (1, 0, -1) \rightarrow S = 1 \Rightarrow {}^3\Sigma$
   - $M_S = 0 \rightarrow S = 0 \Rightarrow {}^1\Sigma$

Terms corresponding to equivalent electrons

- A complete shell $(\sigma^2, \pi^4, \delta^4, ...)$ corresponds to $\Lambda = S = 0 \mapsto {}^1\Sigma$.
- A shell π^3 gives rise to the same terms as a shell π. The same applies to shells δ, ϕ, ...